tion of the Grignard reagent is a general one, and seems to be much superior to their preparation in ether. Mercuric chloride is but slightly soluble in ether and is inclined to cake in the reaction mixture,[6] while 100 g. of mercuric chloride can readily be dissolved in 100 ml. of tetrahydrofuran. Furthermore, prolonged periods of heating to obtain satisfactory yields[7] are no longer necessary. In several attempts to prepare di-*n*-propylmercury in good yield in ether after the improved method of Gilman and Brown,[8] the highest yield obtained was 57%. Marvel and Gould[6] report a 51% yield of this compound in ether solution. A single trial using tetrahydrofuran gave a 75% yield of the di-*n*-propylmercury.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen. The tetrahydrofuran employed was predried over sodium hydroxide pellets and distilled from sodium wire.

Dicyclopropylmercury. Cyclopropylmagnesium bromide was prepared in tetrahydrofuran from magnesium turnings and cyclopropyl bromide, which was made according to the method of Roberts and Chambers.[9] To 4.6 g. (0.19 mole) of magnesium in a 250 ml. 3-necked flask equipped with stirrer, water-cooled condenser, thermometer, and dropping funnel was added just enough tetrahydrofuran to cover the surface of the magnesium and approximately 3 ml. of cyclopropyl bromide. Reaction was thoroughly initiated by heating the solution to reflux for several minutes. The remaining 0.19 mole of cyclopropyl bromide, dissolved in 100 ml. of tetrahydrofuran, was added over a period of 1 hr. with the temperature of the reaction being held at 15–20° with an ice water bath to prevent coupling. Reaction was completed by heating the solution to between 50–60° for 1 hr.

To this Grignard solution was added dropwise with stirring a solution of 20.6 g. of mercuric chloride (80% of theory) in 50 ml. of tetrahydrofuran. After the addition was completed the solution was gently refluxed overnight. At the end of this time the solution was cooled and hydrolyzed with 50 ml. of water. Stirring was continued during the entire heating and hydrolysis. The liquid was separated from the pasty precipitate by suction filtration, the organic layer extracted with ether, washed with several portions of water, and dried over anhydrous magnesium sulfate. After preliminary stripping off of the organic solvent at atmospheric pressure using a water bath, the remaining liquid was transferred to a small distillation flask and vacuum distilled. 13.7 g. of dicyclopropylmercury was obtained (64% of theory), b.p. 110–112° at 18 mm.

Anal. Calcd. for $C_6H_{10}Hg$: C, 25.49; H, 3.57. Found: C, 25.56; H, 3.72.

Divinylmercury. Vinylmagnesium bromide was prepared from 30.4 g. (1.25 mole) of magnesium turnings and excess vinyl bromide in 500 ml. of tetrahydrofuran according to the method of Normant.[10] To the Grignard solution in a 2-l. flask equipped as previously described was added dropwise a solution of 136 g. of mercuric chloride (80% of theory) in 200 ml. of tetrahydrofuran. Addition was accomplished over a period of 1 hr. with stirring at a temperature of about 60°. After completion of addition the solution was heated for 1 hr. with stirring at 60° with an infrared lamp. The solution was then allowed to cool, and the remaining Grignard decomposed by hydrolysis with 250 ml. of water. Work-up proceeded as before with the exception that the organic solvent was separated from the rather volatile divinylmercury by use of a Rinco Rotary Evaporator. Using a water aspirator and a water bath at 30° the solvent came off at about 20 mm. The evaporation was discontinued when the pressure fell abruptly to 12–14 mm. The remaining liquid was distilled under vacuum through a 10 cm. Vigreux column by use of a water bath. 76.8 g. of divinylmercury (60% of theory) was obtained, b.p. 48–50° at 14 mm.

Anal. Calcd. for C_4H_6Hg: C, 18.86; H, 2.38. Found: C, 18.81; H, 2.58.

Because of its volatility, divinylmercury should be handled with extreme care in a good hood, as the dangerous toxicity of organomercury compounds is well known.[11] Divinylmercury readily decolorizes potassium permanganate solution while dicyclopropylmercury does not.

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(6) C. S. Marvel and V. L. Gould, *J. Am. Chem. Soc.*, **44**, 153 (1922).

(7) H. Gilman and R. Brown, *J. Am. Chem. Soc.*, **51**, 928 (1929).

(8) H. Gilman and R. Brown, *J. Am. Chem. Soc.*, **52**, 3314 (1930).

(9) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 3176 (1951).

(10) H. Normant, *Bull. soc. chim. France*, 728 (1957).

(11) Sax, *Handbook of Dangerous Materials*, Reinhold Publishing Corp., 1951, p. 236.

Use of Chlorides in the Preparation of Organic Sulfides

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The reaction of alkyl bromides or iodides with sodium sulfide to give organic sulfides is well known.[2] Alkyl chlorides, though frequently more readily available than the bromides or iodides, are seldom employed.

Our research activities required a sample of bis-(2-ethylhexyl) sulfide. Since this material does not appear to be listed in the literature, we sought a method of preparation, preferably one suitable for scaling up, and which utilized commercially available intermediates. Since 2-ethylhxeyl bromide and iodide were not readily available, the usual method of allowing an alkyl bromide or iodide to react with sodium sulfide in aqueous or alcoholic solution was not applicable.[3] The reaction of 2-ethylhexyl

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(1) Present address: Ethyl Corp., Baton Rouge, La.

(2) See (*a*) D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3627 (1951); and (b) R. W. Bost and M. W. Conn, *Org. Syntheses*, **Coll. Vol. II**, 547 (1943).

chloride with sodium sulfide was inviting if suitable conditions could be found for causing it to take place. As expected, this reaction was very slow in aqueous or alcoholic solution. The use of ethylene glycol as a solvent gave a much more satisfactory procedure (see Experimental). The yield of bis-(2-ethylhexyl) sulfide from such a run was 76%.

As a further check on the usefulness of ethylene glycol as a solvent in the reaction of an organic chloride with sodium sulfide, a run was carried out employing 1,4-dichlorobutane. This reaction proceeded smoothly giving a 67% yield of tetramethylene sulfide.

Though our examples illustrating the usefulness of ethylene glycol as a solvent in the preparation of organic sulfides are limited, it appears likely that the method is of general applicability. Since we do not plan further investigation along this line, we feel it is desirable that we report our results for those who may find the method of interest.

EXPERIMENTAL

The starting materials were obtained from commercial sources and were used without purification. Boiling points are uncorrected. Fractionations were carried out through an 80-cm. Podbielniak-type column similar to that described by Cason and Rapoport.[4]

Bis(2-ethylhexyl) sulfide. A two-phase mixture of 74.3 g. (0.5 mole) of 2-ethylhexyl chloride, 60 g. (0.25 mole) of sodium sulfide nonahydrate, and 200 ml. of ethylene glycol was maintained at the boiling point (about 135°) under reflux for 24 hr. The course of the reaction was followed by removing a small sample of the upper phase from time to time to time and checking its refractive index. This property showed a moderately rapid increase during the early stages but had essentially ceased changing at the end of the heating period. At this point the upper layer was separated, washed twice with water, and dried over calcium chloride. Fractionation gave a forerun of about 10 g. of 2-ethylhexyl chloride, followed by 49 g. (76%) of nearly colorless product at 178–179° (23 mm.), n_D^{25} 1.4622.[5]

Anal. Calcd. for $C_{16}H_{34}S$: C, 74.34, H, 13.26, S, 12.40. Found: C, 74.46, H, 13.09, S, 12.24.

On a similar run to that described above, except that 200 ml. of ethanol was used in the place of the ethylene glycol, it was observed that the ethanol remained primarily in the upper phase with the alkyl chloride at the start of the reaction. As the reaction proceeded (reflux temperature, about 80°), the lower phase increased in volume and salts separated out, giving some tendency to bump. After a 24-hr. reflux period the reaction was worked up essentially as described above. Fractionation gave a forerun followed by 46 g. (71%) of bis(2-ethylhexyl) sulfide at 162–163° (12 mm.).

Tetramethylene sulfide. A mixture of 127 g. (1 mole) of 1,4-dichlorobutane and 240 g. (1 mole) of sodium sulfide nonahydrate was heated under reflux for 7 hr. The refractive index of the upper layer increased from n_D^{20} 1.4552 to n_D^{20} 1.4560 during this time, indicating very little reaction. At this point, 100 ml. of ethylene glycol was added and heating was continued for 16 hr. The refractive index of the upper layer (which was unchanged by the addition of the ethylene glycol since this component went into the lower phase) increased rapidly during this time to a final value of n_D^{20} 1.5038. At this point the upper layer was separated, washed twice with 20% sodium chloride solution, and dried over calcium chloride. Fractionation gave a yield of 59 g. (67%) of tetramethylene sulfide at 120–121°, n_D^{20} 1.5043 (lit.,[6] b.p. 121.2°, n_D^{20} 1.5047).

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[3] Since 2-ethylhexanol is commercially available, the method of preparation of sulfides utilized by F. Drahowzal and D. Klamann [*Monatsh.*, **82**, 970 (1951)] involving the reaction of an alkyl-4-toluenesulfonate with sodium sulfide was seriously considered. However, this would have involved the preparation of 2-ethylhexyl-4-toluenesulfonate as an intermediate, and was abandoned in favor of the direct reaction of the alkyl chloride with sodium sulfide.

[4] J. Cason and H. Rapoport, *Laboratory Text in Organic Chemistry*, Prentice-Hall, Inc., New York, N. Y., 1950, p. 238.

[5] On one run similar to that described here, except that no ethylene glycol was added, many hours of refluxing gave very little reaction. Fractionation of the top phase gave a recovery of 75% of the 2-ethylhexyl chloride and revealed no significant amount of the desired sulfide. A small forerun was not identified. When ethylene glycol was added to the run described above, it dissolved essentially completely in the sodium sulfide nonahydrate phase, giving a higher reflux temperature and possibly increasing the amount of alkyl chloride which dissolved in this phase.

[6] E. V. Whitehead, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3632 (1951) made use of the dibromide in the preparation of this compound.

The Polymerization and Cyclization of Allyldimethylsilane

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Mironov and Petrov have recently described[1] the synthesis and polymerization of certain silanes containing an unsaturated organic group and hydrogen joined to the same silicon atom. They reported, however, that they were unable to cause the polymerization of allyldimethylsilane under their experimental conditions (refluxing in the presence of 15% platinized carbon). We wish to report that we have successfully polymerized this monomer as well as effected the formation of a cyclic dimer from it.

Allyldimethylsilane was synthesized under high dilution conditions by a Grignard reaction, starting from dimethylchlorosilane, allyl bromide, and magnesium. The resulting monomer was heated under reflux, in the absence of solvent, with a 0.06% platinum-on-carbon catalyst.[2] Polymerization proceeded smoothly to yield a colorless, moderately viscous liquid, similar in appearance to the di-

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[1] V. F. Mironov and A. D. Petrov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 383 (1957).

[2] G. H. Wagner (to Union Carbide and Carbon Corp.), U. S. Patent **2,637,738**, May 5, 1953.